Aerosol assisted chemical vapour deposition of germanium thin films using organogermanium carboxylates as precursors and formation of germania films

ALPA Y SHAH, AMEY WADAWALE, VIJAYKUMAR S SAGORIA, VIMAL K JAIN*, C A BETTY and S BHATTACHARYA[†]

Chemistry Division, [†]Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Abstract. Diethyl germanium *bis*-picolinate, [Et$_2$Ge(O$_2$CC$_5$H$_4$N)$_2$], and trimethyl germanium quinaldate, [Me$_3$Ge(O$_2$CC$_9$H$_6$N)], have been used as precursors for deposition of thin films of germanium by aerosol assisted chemical vapour deposition (AACVD). The thermogravimetric analysis revealed complete volatilization of complexes under nitrogen atmosphere. Germanium thin films were deposited on silicon wafers at 700°C employing AACVD method. These films on oxidation under an oxygen atmosphere at 600°C yield GeO$_2$. Both Ge and GeO$_2$ films were characterized by XRD, SEM and EDS measurements. Their electrical properties were assessed by current–voltage (I–V) characterization.

Keywords. Organogermanium; germanium thin films; AACVD; XRD.

1. Introduction

Germanium has gained a renewed interest in electronics industry due to its lower bandgap energy (0·67 eV) and higher electron and hole mobilities than silicon (Sze *et al* 1981). Germanium based thin films find numerous applications in micro-electronic devices. Germanium oxide (GeO$_2$) is used as blue photoluminescent materials (Zacharias and Fauchet 1998; Trukhin 2009; Liu *et al* 2010), whereas GeO$_2$ based glasses having high refractive index are used for nano connections in optoelectronic devices (Kim *et al* 2003).

Recently, several synthetic approaches have emerged to prepare germanium and germanium oxide nanocrystals and thin films. For the preparation of GeO$_2$ nanocrystals, Ge(OR)$_4$ (R = Pr^i or Bu^t) are frequently employed (Kim *et al* 2003; Shah *et al* 2010). Several strategies have been adopted for deposition of germanium thin films, among them CVD has emerged as a promising technique due to its versatility. The most commonly used germanium precursor is the pyrophoric germane [GeH$_4$] (Kohlhase *et al* 1991; Mukherjee *et al* 2001; Wang *et al* 2004). Organogermanium compounds like [Cp*GeH$_3$] (Dittmar *et al* 2001), [Et$_n$GeH$_{4−n}$] (n = 1–4) (Pola *et al* 1992b), [Bu^{i}GeH$_3$] (Woelk *et al* 2006), [Bu^{i}GeCl$_3$] (Woelk *et al* 2006), [Me$_3$GeCl] (Woelk *et al* 2006), [Et$_4$Ge] (Boucham *et al* 1998), [Me$_3$Ge(OEt)] (Fajgar *et al* 1995), [(PhGeO$_{1·5}$)$_n$] (Henderson *et al* 2010) and cyclic germylene (Veprek *et al* 1996) have been employed as precursors in CVD methods. Tetramethoxy germane, [Ge(OMe)$_4$] (Pola *et al* 1992a;

Henderson *et al* 2010), has been used for the preparation of organogermanium films by laser induced deposition. The compounds like [Me$_3$Ge(OEt)] and [Ge(OMe)$_4$] give films contaminated with carbon, hydrogen and oxygen (Fajgar *et al* 1995), while the germanium hydride precursors are toxic and pyrophoric whereas chlorinated compounds are corrosive. To overcome these problems, research is directed to design and develop new organogermanium precursors for deposition of germanium films by CVD.

Recently, we have described the synthesis of organogermanium carboxylates and characterized some of them, [Et$_2$Ge(O$_2$CC$_5$H$_4$N)$_2$] (**1**) and [Me$_3$Ge(O$_2$CC$_9$H$_6$N)] (**2**), (scheme 1) by X-ray structural analyses (Shah *et al* 2009). It was considered worthwhile to examine their suitability as precursors for deposition of germanium thin films.

2. Experimental

Organogermanium carboxylates, [Et$_2$Ge(O$_2$CC$_5$H$_4$N)$_2$] (**1**) and [Me$_3$Ge(O$_2$CC$_9$H$_6$N)] (**2**) were synthesized by an earlier reported method (Shah *et al* 2009) and were characterized by NMR spectroscopy. Germanium thin films were deposited on Si substrate (1 × 1 cm) by aerosol assisted chemical vapour deposition (AACVD). Single crystals of silicon wafers (thickness 380 ± 30 μ; with (100) or (111) orientation, boron doped (*p*-type) with resistivity 1–3 ohm-cm) were used for deposition of thin films. Prior to deposition, Si wafers were thoroughly cleaned by standard RCA cleaning procedure. Deposition was carried out on cleaned rough surface.

*Author for correspondence (jainvk@barc.gov.in)
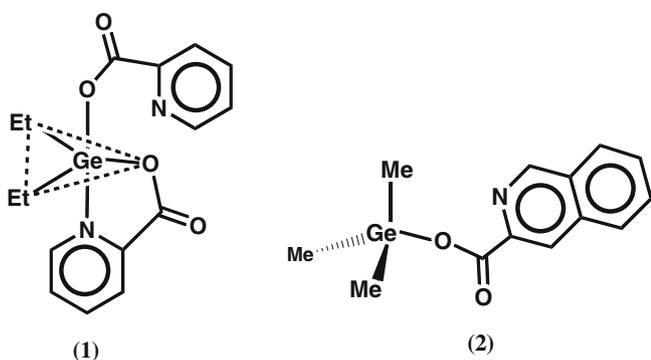
Scheme 1. Structures of organogermanium carboxylates.

In a typical experiment, an organogermanium carboxylate (150 mg) was dissolved in dry benzene (60 ml) in a two-necked round bottom flask, which was connected to a quartz tube placed in a horizontal tube furnace. An aerosol from this solution was generated at room temperature by use of ultrasonic humidifier. The aerosol was transported on to a pre-heated cleaned silicon wafer in a quartz tube by high purity argon flow maintaining a flow rate of 4 L/min. The substrate temperature was monitored by Cr–Al thermocouple. The organic volatile part eliminated from the precursor and the solvent was carried by the argon flow and condensed in a liquid nitrogen trap placed at the end of the reactor. After cooling under argon flow, thin films were characterized by powder X-ray diffraction, EDS and SEM data.

Thermogravimetric analysis was performed on Netzsch STAPC Luxx instrument, which was calibrated with $CaC_2O_4 \cdot H_2O$, with a heating rate of 10°C/min under N_2 atmosphere. Powder X-ray diffraction measurements were done on a Phillips PW 1810 instrument. Scan speed of XRD was $1 \cdot 25°$ min. Surface morphology was studied by scanning electron microscopy on a Kevex/Tescan Vega 2300T/40 instrument. EDS experiments were carried out on a Kevex Instrument. Current–voltage (I–V) and capacitance–voltage (C–V) measurements were carried out to evaluate electrical properties. For the electrical contacts, many gold dots (1 mm dia) were deposited on top of Ge and GeO_2 films using shadow mask. For the I–V and C–V measurements of Si/Ge/Au and Si/GeO_2/Au structures, potentiostat PGSTAT 20 (Echochimie, The Netherlands), was used. Capacitance voltage characteristics of Si/GeO_2/Au structures were obtained from the impedance data measured using a peak-to-peak small signal a.c. voltage of 10 mV at 100 kHz.

To prepare germanium oxide (germania) films, the germanium films were annealed under oxygen atmosphere in a furnace at 600°C for 3 h. Films were characterized as GeO_2 by powder X-ray diffraction, SEM and EDS data.

## 3. Results and discussion

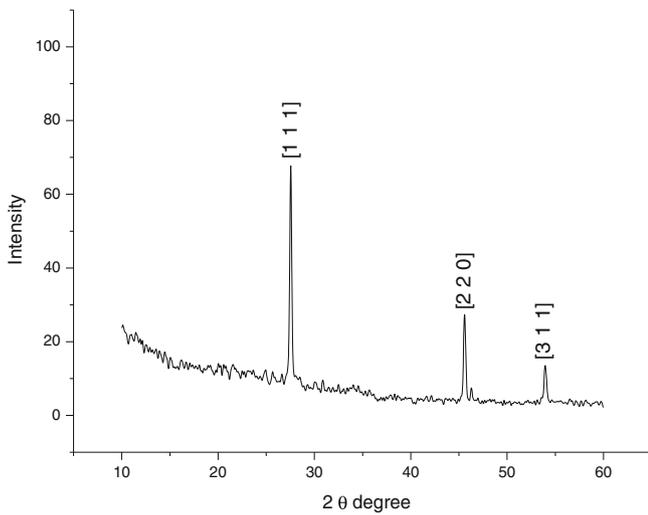Recently, we have described the synthesis of organogermanium carboxylates (Shah *et al* 2009). To evaluate the suitability of these complexes as molecular precursors for deposition of thin films of germanium, structurally characterized compounds, $[Et_2Ge(O_2CC_5H_4N)_2]$ (**1**) and $[Me_3Ge(O_2CC_9H_6N)]$ (**2**), were chosen as precursors. The precursors were crystallized and fully characterized ensuring their high purity. Their high solubility in dry organic solvents to serve as liquid germanium source, which is further converted into an aerosol (almost 100%) by ultrasonic humidifier, allowed us to use them as precursor. Although these complexes are sensitive to moisture, they can be handled in air for a short period and hence ease of handling, which allows CVD experiments without extensive safety equipments. Thus, the use of these precursors is advantageous due to the ease of their preparation, purification, solubility and stability.

Thermogravimetric analysis of these compounds revealed nearly complete weight loss indicating their volatility. DTA curve of $[Et_2Ge(O_2CC_5H_4N)_2]$ indicates that the first endotherm corresponding to melting of the compound is accompanied by nearly complete volatilization (~98% weight loss). In the case of $[Me_3Ge(O_2CC_9H_6N)]$, the first endotherm at 92°C corresponds to melting of the compound followed by a single step volatilization (figure 1). In an attempt to pyrolyze these compounds in a furnace at 300°C under an argon atmosphere, complete vaporization was noticed.
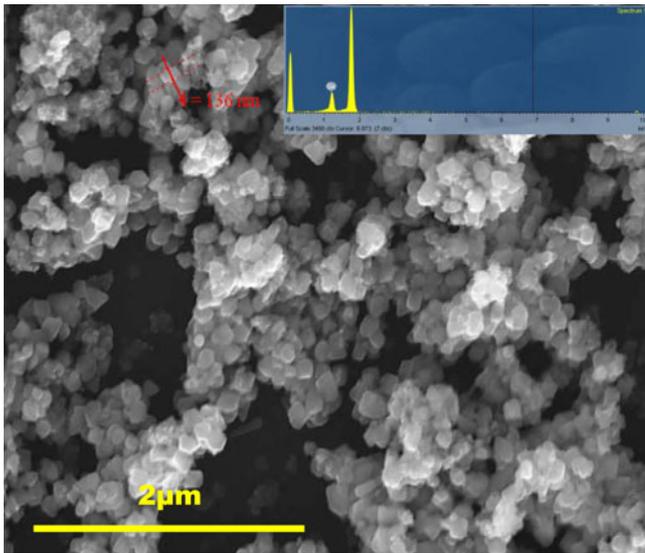
Aerosol assisted chemical vapour deposition (AACVD) of $[Et_2Ge(O_2CC_5H_4N)_2]$ (**1**) and $[Me_3Ge(O_2CC_9H_6N)]$ (**2**) at 700°C on boron-doped *p*-type silicon wafers resulted into germanium films. XRD patterns of the films obtained from these compounds were similar. XRD patterns were interpreted for the cubic phase with preferential orientation in (110), (220) and (311) planes (figure 2), which were in good agreement with the reported values for germanium (JCPDS
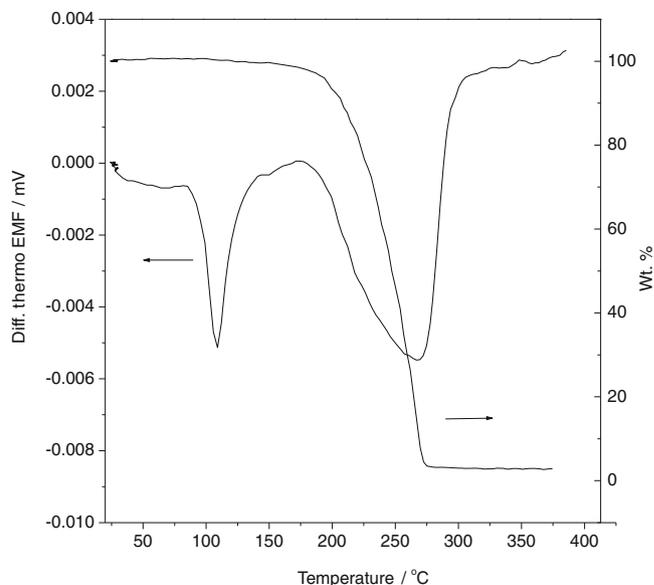
Figure 1. TGA curve of $[Me_3Ge(O_2CC_9H_6N)]$.

Figure 2. XRD pattern of Ge films obtained from [Me$_3$Ge(O$_2$CC$_9$H$_6$N)].

Figure 4. XRD pattern of GeO$_2$ obtained by heating Ge film at 600°C in furnace under static oxygen.

Figure 3. SEM image of Ge thin films obtained from [Me$_3$Ge(O$_2$CC$_9$H$_6$N)]. Inset shows EDS spectrum of Ge thin film.
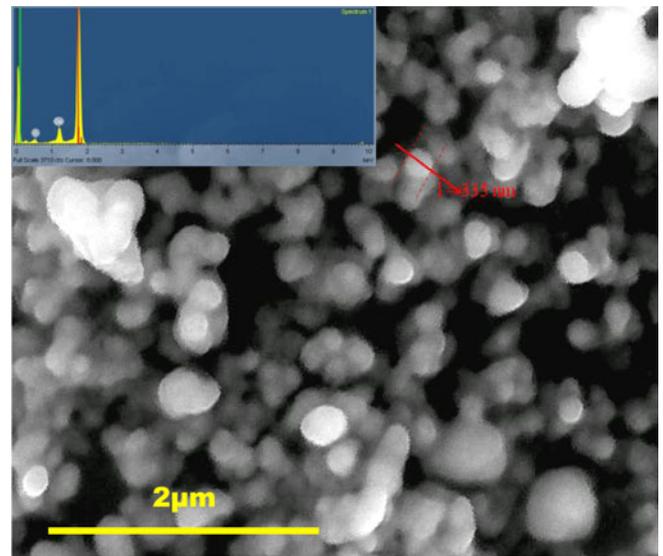
Figure 5. SEM of GeO$_2$ thin films obtained by heating Ge film at 600°C in furnace under static oxygen. Inset shows EDS spectrum of Ge thin films oxidized to GeO$_2$.

card#:04-0545) (Kim *et al* 2003). The measured reflections were of high intensity with narrow peak widths indicating crystalline nature. The average size of germanium nanoparticles estimated by the Scherrer formula is 17 nm and 40 nm when precursors (**1**) and (**2**) are used, respectively. EDS analysis revealed deposition of germanium. No contamination species were observed within the sensitivity of the instrument. Scanning electron microscopic (SEM) images revealed agglomeration of germanium nanoparticles which were polygonal in shape (sizes: < 200 nm) (figure 3). Germanium films prepared from other organometallic precursors, e.g. [Me$_3$Ge(OEt)] by laser induced decomposition, yield germanium films contaminated with oxygen and carbon (Fajgar *et al* 1995). The films prepared from [Cp*GeH$_3$] (Dittmar

et al 2001) are contaminated with carbon (8%) whereas GeH$_4$ requires high decomposition temperature (1250°C) (Mukherjee *et al* 2001).

The germanium films when heated at 600°C in a furnace under oxygen, lead to the formation of germanium oxide (germania) films. The selected reflections were indexed on the basis of hexagonal GeO$_2$ and are marked in figure 4. The unit cell parameters obtained from the observed data [$a = 4·94$ (1) Å and $c = 5·61$ (2) Å] are in good agreement with reported values for hexagonal GeO$_2$ (JCPDS card#:83-0544). A peak due to Ge (1 1 1) (JCPDS card#:04-0545) was also found in GeO$_2$ film indicating incomplete oxidation. However, quantitative analysis of EDS (Ge/O atomic ratio, 33·33:66·66, which is 1:2) confirmed the formation of
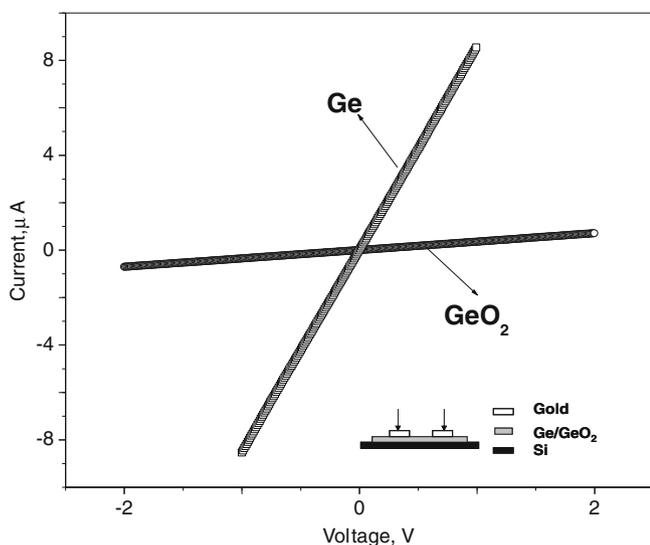
Figure 6. Typical *I–V* characteristics of Si/Ge/Au and Si/GeO$_2$/Au co-planar structures. Inset shows schematic of co-planar structure.

germanium oxide. Oxidation of Ge films in an oxygen atmosphere has been described earlier (Ko *et al* 2008). A gradual oxidation of Ge to GeO$_2$ with increasing annealing time has been reported earlier (Ko *et al* 2008). The average size estimated by Scherrer's formula of our GeO$_2$ nanoparticles is 33 nm. While comparing SEM images of Ge and GeO$_2$ films, the former had well defined grain boundaries while the grain boundaries for the latter were diffused (figure 5).

Electrical properties of Ge and GeO$_2$ have been studied by *I–V* measurements. On a Ge or GeO$_2$ film (1×1 cm), many gold contacts (diameter, $\sim$1 mm) separated by 2 mm were deposited on the growth side. *I–V* characteristics of both the structures, Si/Ge/Au and Si/GeO$_2$/Au, were carried out using co-planar structure between various pairs of adjacent gold dots on the same film. These measurements showed ohmic behaviour for both Ge and GeO$_2$ films (figure 6). The resistivity values calculated for Ge and GeO$_2$ films were 1·44 kΩ-cm and 35·6 kΩ-cm, respectively. Capacitance voltage studies of Si/GeO$_2$/Au structures (not shown) gave constant capacitance of 1·28 pF indicating the characteristics of a typical insulator.

4. Conclusions

Germanium thin films have been deposited by AACVD using di- and tri-organogermanium carboxylates. These films can be oxidized to germania using conventional heating in oxygen ambient. Ge and GeO$_2$ films have been characterized by various techniques. It has been demonstrated that high quality Ge and GeO$_2$ films can be obtained conveniently by using organogermanium carboxylates.

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